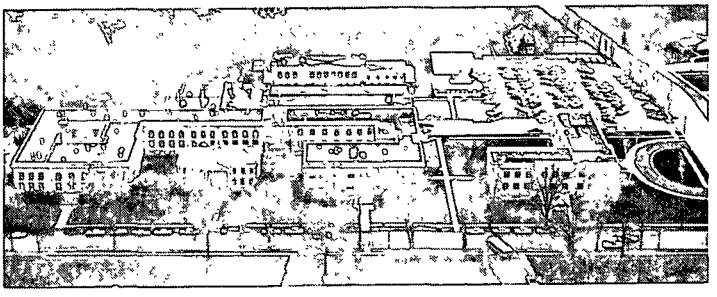

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# RECOVERY BOILER AIR PORT CORROSION

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# Recovery boiler air port corrosion

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## ABSTRACT

Corrosion of recovery boiler air ports is reviewed. Localized corrosion at recovery boiler air ports has been attributed to condensed sodium hydroxide. Reported observations are consistent with an alternative mechanism involving corrosion by chloride and pyrosulfate.

## INTRODUCTION

Air is introduced into the recovery boiler through ports in the water cooled walls of the boiler. The primary set of ports is located at bed level and the secondary and tertiary sets are above that. Corrosion of air ports has been a chronic problem of recovery boilers. In the 1960s, Plumley, Lewis and Tallent (1) concluded, after field and lab studies, that wastage of carbon steel observed near air ports might be due to a gas-solid reaction, perhaps involving the localized concentration of oxygen, carbon dioxide and sulfur-containing gases. In an effort to obtain improved resistance to oxidation/sulfidation, gas phase research was carried out in Scandinavia to look at various steels over a range of temperatures and gas composition (2). It was concluded that chromium steels possessed superior resistance to corrosion. The subsequent use of stainless steels for composite tubes has successfully reduced fireside corrosion rates in kraft recovery boilers.

Severe corrosion has occurred on tube surfaces under deposits on the cold side of carbon steel tubes. This corrosion has been attributed to condensation

of sodium hydroxide at lower temperatures. Clement (3), investigating corrosion on the windbox side of flat stud boilers, argued that corrosion was due to reaction of iron, condensed NaOH and $O_2$ to form $Fe_2O_3$ and then nonprotective $NaFeO_2$. Hydroxide condensation was further implicated by Bruno (4).

Stainless steel composite tubes have also suffered localized wastage of the stainless steel primarily near air ports of high pressure boilers (5). Corrosion and cracking were described further by Wensley (6) and were attributed to the condensation of hydroxide. The stainless steel is attacked more severely than the carbon steel. Although this is commonly called cold side corrosion, attack frequently extends onto the hot side of the tubes. Barna and Rogan (7) have reported on the appearance and occurrence of corrosion of composite tubes at port openings. They considered that the corrosion process depends on formation of crevices that have the capability of accumulating deposits and that form a nongas-tight seal between the furnace and casing side of the tubing. Under these deposits, hydroxide vapors could condense to form a molten phase at the deposit/substrate interface and this NaOH would preferentially corrode the stainless steel. Figures 1 and 2 illustrate the locations susceptible to corrosion in some older B & W composite air port designs. Wensley (8) reported that tube cladding wastage and the preferential corrosion of the stainless cladding from flat studs often occurred together. He also noted that those openings which evidently experienced higher temperature conditions in service, resulting in both flat stud burn-back and flat stud notch cracking, were less likely to exhibit pronounced stainless cladding wastage. Conversely, areas of cladding wastage experienced less flat stud burn-back and notch cracking. This suggests that stainless steel removal is a low temperature phenomenon. Wensley also reported measurements of the waterwall tube temperatures between the primary and

secondary air ports which were between 300 and 350 C (570-660 F), as measured by chordal thermocouples, confirming that the temperatures of the tubes are fairly low. In a failure analysis of a cracked composite recovery boiler tube, Odelstam (9) determined that that tube had reached extreme temperatures as high as 500-550 C (930-1020 F). A steep temperature gradient would be expected within the deposit or frozen smelt layer in any case.

Figures 1 and 2 here

Despite the fact that corrosion around the air ports is associated with deposits, the conditions in deposits are poorly defined due to the difficulty of sampling and analysis. Retrieval of representative corrosion deposits is very difficult, especially because corrosion is localized and unpredictable. Bruno (4) had perhaps the most to report regarding deposits (formed on carbon steel in lower pressure boilers). Sulfur content of these deposits was very low. He found that deposits from the Iggesund recovery boiler began to melt at 250 C (480 F). Deposits containing 12% NaOH were encountered in a boiler (280 C, 64 bar) near the primary and secondary air ports. Sodium sulfide (2.1%) and sodium sulfate (2.8%) were low, although other analyses of deposits from around air ports showed higher sulfate concentrations. Clement (3) described chemical accumulations at air ports, with a black and red deposit ($NaFeO_2$) next to the tube, yellow and green layers outside that, and extending into a gray layer of unreacted "Hydrochrome" refractory material. The pH was about 12 and sulfur (as $SO_3$) was less than 2%. The temperature in the area was about 315 C (600 F). Odelstam et al. (10) have provided analyses of deposits showing very high NaOH composition, although the method of analysis for NaOH was not described.

**Hydroxide Corrosion**

In explaining the preferential corrosion of stainless steel from composite tubes, Odelstam (9) referenced work by Rahmel which indicated that carbon steel is more resistant to molten hydroxide than are Cr and CrNi steels. The corrosion rate depends on the $Na_2O_2$ content in the pure NaOH melt which in turn depends on oxygen and steam partial pressure in the gas above the melt. The chromium is especially reactive to form chromate ($Na_2CrO_4$) via:

$$4\ NaOH + Cr_2O_3 + 3/2\ O_2 \rightarrow 2\ Na_2CrO_4 + 2\ H_2O \qquad (1)$$

This reaction would flux the protective chromium oxide passive layer from the stainless steel, causing rapid corrosion. The hydroxide corrosion mechanism is summarized in Figure 3.

Figure 3 here

The NaOH condensation mechanism has been recently summarized by Odelstam et al. (10). According to the theory, the NaOH may condense if the hot furnace gas is cooled rapidly and then mixed with low (< 1 ppm) $CO_2$ air. In areas in contact with the furnace gas with high $CO_2$ concentration, the NaOH would react to form harmless carbonates and sulfates. Laboratory results were described in which severe corrosion of 304L SS occurred at the interface between molten $NaOH/Na_2CO_3$ and air. Compared to the 304 SS, type 310 stainless steel corroded less, and carbon steel less than either stainless steel. They also reported tests confirming that NaOH and $Cr_2O_3$ react to form $Na_2CrO_4$, and presented analysis of corrosion deposits containing high NaOH concentrations.

Although the observed corrosion is consistent with NaOH attack, there is no direct evidence of NaOH. The present authors have some reservations regarding

the condensation of NaOH. Sodium hydroxide fume is difficult to produce in the recovery boiler (11). Pejryd and Hupa (12) have made equilibrium calculations for the gas composition in the kraft furnace which show that NaOH vapor is a stable species only at temperatures above 800 C (1470 F). However, in the temperature range from 800 to 1300 C (1470-2370 F), the equilibrium $CO_2$ concentration is several orders of magnitude greater than the equilibrium NaOH concentration and it is unlikely that NaOH could condense in such an atmosphere without reacting with the $CO_2$ to form $Na_2CO_3$.

Many analyses of corrosion deposits from air ports have not provided evidence of NaOH condensation. Furthermore, the high NaOH levels which have been reported may be artifacts of the chemical analysis procedure used for analyzing the deposits. The high NaOH levels may form by the reverse of reaction (1) during an analytical titration procedure. Another possibility is that carbonates in the smelt may react with ferric oxide corrosion product via:

$$Na_2CO_3 + Fe_2O_3 \rightarrow 2\ NaFeO_2 + CO_2 \qquad (2)$$

When the smelt deposit is dissolved in water for analysis, it would react:

$$2\ NaFeO_2 + 2\ H_2O \rightarrow 2\ NaOH + Fe_2O_3.H_2O \qquad (3)$$

resulting in an elevated pH and indicating the presence of NaOH. These reactions are the basis of the DARS chemical recovery process.

**Corrosion by Pyrosulfate**

Recent research by Cameron (11) indicates that KCl and NaCl are major volatile species from melts similar to those found within the recovery furnace and that very little NaOH vapor is produced. Liden and Pejryd (13) have noted that KCl(g) and NaCl(g) may be emitted in about equal amounts, even though potassium

is a minor constituent of the liquor. These salts may deposit on cooler surfaces within the furnace. On exposure to $SO_3$ or $SO_2$, they would be expected to form pyrosulfates $Na_2S_2O_7$ and $K_2S_2O_7$ via the equations:

$$2\ KCl\ (s) + 2\ SO_3\ (g) + 1/2\ O_2 \longrightarrow K_2S_2O_7\ (l) + Cl_2\ (g) \qquad (4)$$

$$2\ KCl\ (s) + 2\ SO_2\ (g) + 3/2\ O_2 \longrightarrow K_2S_2O_7\ (l) + Cl_2\ (g) \qquad (5)$$

Pyrosulfate formation would be anticipated at the air ports where higher $SO_2$ and $SO_3$ levels would be favored. Therefore, pyrosulfate should be considered as a possible corrosive agent within the recovery boiler. Chloride concentrations in corrosion deposits were low according to Bruno (4), which would be consistent with volatilization of $Cl_2$ via Eq. (4) and (5).

Although pyrosulfate is known to be a corrosive agent (14,15,16) it has not been considered as a potential agent for the corrosion observed with composite tubes. This appears to be a result of equilibrium studies by Backman and Hupa (17) which show that $Na_2S_2O_7$ is unstable at the $SO_2$ levels and temperatures found within a recovery boiler. Backman and Hupa concluded that $Na_2S_2O_7$ could only occur if the $SO_x$ concentration exceeds 5000 ppm. Since the $SO_2$ concentration in kraft furnaces is in the range of 50 to 500 ppm, $Na_2S_2O_7$ would be expected to be unstable and therefore was eliminated from consideration as a corrosive agent. These conclusions differ from the findings of Coats, Dear and Penfold (18). They have measured the relation between the partial pressure of $SO_3$ and melting point temperatures of alkali pyrosulfates. For example, at 425 C (800 F) about 2500 ppm of $SO_3$ is necessary to form $Na_2S_2O_7$ or about 150 ppm $SO_3$ to form $K_2S_2O_7$. This points to the possible importance of potassium to corrosion, as its pyrosulfate is more easily formed than is sodium pyrosulfate.

While $Na_2S_2O_7$ may be unstable at the $SO_x$ levels in the recovery furnace, there are conditions under which it will form. Fielder et al. (19) and Anderson and Hung (20) have shown that NaCl will react rapidly with $SO_2$ or $SO_3$ at 400 C and $SO_x$ level less than 1000 ppm to form $Na_2S_2O_7$ via Eq. (2). Fielder et al. (19) found that on exposure to $SO_2$-$SO_3$-$O_2$, a NaCl sample was essentially molten $Na_2S_2O_7$ after 10 min at 401 C (754 F). By raising the temperature to 500 C (930 F) in a stream of $O_2$, the $Na_2S_2O_7$ slowly converted to a nonadhering film of $Na_2SO_4$. They proposed that for the temperature range 401 to 450 C (750 to 840 F), molten $Na_2S_2O_7$ is the principal film product that is formed when NaCl is exposed to the oxides of sulfur. Reid has noted that equilibrium favors $SO_3$ over $SO_2$ below 482 C (900 F). This is confirmed by Lees and Whitehead (21). Thus as furnace gas cools, $SO_3$ may be more stable and it may react via Eq. (4).

The corrosion in the area of the air ports in the recovery boiler may result from pyrosulfate. Based on the work of Fielder et al. (19), and the conclusions of Cameron (11) that NaCl and KCl are the major volatile species in the recovery boiler, production of pyrosulfate appears to be possible. This would occur in areas where the temperature is in the range 400 to 450 C (750 to 840 F) and chloride, $SO_3$ and $O_2$ are present. On the cold side of the waterwall, and in areas in contact with air these conditions may be present. The molten nature of the pyrosulfate would account for the appearance of the tube wastage where it is suggestive of erosion by a liquid phase. Backman, Hupa, and Hyoty (17) have noted that $Na_2S_2O_7$-$K_2S_2O_7$ mixtures might have a low eutectic temperature (down to 280 C). Lees and Whitehead (21) found that a 50:50 $K_2S_2O_7$/$Na_2S_2O_7$ mixture formed a complete liquid above about 325 C (615 F) which is within the range of tube temperatures reported by Wensley (8).

The role of pyrosulfates in corrosion has been reviewed by Reid (14). Vaughan et al. (16) have suggested:

$$K_2S_2O_7 + 3\ Fe \rightarrow Fe_2O_3 + FeS + K_2SO_4 \qquad (6)$$

Work by Corey, Cross and Reid (15) has indicated that at tube-metal temperatures of 425 C (800 F), pyrosulfates probably contribute to metal loss.

$$3\ Na_2S_2O_7 + Fe_2O_3 \rightarrow 3\ Na_2SO_4 + Fe_2(SO_4)_3 \qquad (7)$$

$$4\ Na_2S_2O_7 + Fe_3O_4 \rightarrow 4\ Na_2SO_4 + FeSO_4 + Fe_2(SO_4)_3 \qquad (8)$$

$$3\ Na_2S_2O_7 + Fe_2O_3 \rightarrow 2\ Na_3Fe(SO_4)_3 \rightarrow 3\ Na_2SO_4 + Fe_2O_3 + 3\ SO_3 \qquad (9)$$

Removal of the oxide layers would expose the underlying steel to rapid oxidation and sulfidation. Nevertheless, pyrosulfates have not been found in corrosion products of boilers in concentrations high enough to be identified by x-ray diffraction. However, they may decompose prior to analysis. Corrosion by pyrosulfates would be restricted to a range from 400-480 C (750-900 F) if the pyrosulfate forms on the tube. It may form a molten phase at tube temperatures if present as some eutectic mixture. The pyrosulfate corrosion mechanism is summarized in Figure 4.

Figure 4 here

Evidence from coal-fired boilers has pointed to a pyrosulfate mechanism of corrosion in conditions similar to those at recovery boiler air ports. Lees and Whitehead (21) have described corrosion on 25Cr20Ni stainless steel composite tubes used in coal boilers. The steel is attacked by alkali metal sulfates under critical environmental conditions which favor the stability of high $SO_3$ concentrations. They reported that significant pitting damage occurred at

specific boiler locations where enrichment of $SO_3$ was possible, for example, around a gas sampling port and at the interstitial position of tube contact in a 'tangent' wall, where air has easy access from the casing side. The presence of sulfate was linked with the development of pits; however, high corrosion rates occurred where the sulfate layer had been separated from the 25Cr20Ni steel by a thick oxide/sulfide scale. The behavior of 25Cr20Ni steel was in contrast to that of mild steel, which experienced less corrosion in regions where air locally attenuated the otherwise reducing environment. Preferential corrosion of stainless steel similar to that observed in recovery boilers apparently is possible with pyrosulfates.

Pure Na/K sulfate mixtures were found in specific stoichiometries in deposits on the 25Cr20Ni steel, as with mild steel, but on the stainless steel they were in intimate contact with the metal, especially adjacent to pitting. X-ray microanalysis of the sulfatic deposits at these locations yielded a (Na+K):S ratio of 1:1, which is equivalent to pyrosulfate stoichiometry. Other elemental constituents were occasionally observed such as Pb, Cu, Zn and Fe. Trace pyrosulfates formed within simple sulfates on regions on the tube, adjacent to uncorroded metal, where the measured temperature was 350-450 C (660-840 F) and where tertiary air ingress was apparent.

Lees and Whitehead were uncertain why 25Cr20Ni steel was more susceptible than carbon steel since $Cr_2O_3$ did not dissolve well in $K_2S_2O_7$ at 450 C (840 F), whereas $Fe_3O_4$ did. They speculated that perhaps $Cr_2O_3$ does not form on 25Cr20Ni and a duplex scale of Cr/Ni spinel and $Fe_3O_4$ results. The spinel may be less stable. On the other hand, pyrosulfates are effective fluxes used in the analysis of chromium ores (22). The reason why mild steel corrosion was not primarily associated with sulfate deposition may have been due to the reduction of the

temperature gradient in the deposit by formation of the thick corrosion scale. With 25Cr20Ni steel, once the thin oxide had been penetrated by the sulfatic attack, reformation might be difficult in the HCl atmosphere despite the lower subsequent reactivity with the sulfate. In this way, chlorine was implicated in the corrosion process. They found chlorine in lower concentrations in 25Cr20Ni scales than on mild steel, although it was concentrated at the scale/metal interface. Layered deposits were formed on the 25Cr20Ni steel, with alternating broad dark bands and narrow light bands. The light bands were of similar composition to the complex dark bands, but contained a far larger proportion of transition metals. This striation formation was thought to be consistent with a cyclic mechanism of attack associated with periodic oxide fluxing, Cr depletion of the metal subsurface due to adjacent sulfates and then attack by HCl, with the resultant corrosion product becoming incorporated into an existing thick deposit of simple sulfates. This would depend on an oxygen excess for sulfatic attack and oxygen deficiency for HCl attack.

Miller et al. (23) measured corrosion rates of steels in a variety of salt compositions with synthetic flue gas at temperatures down to 316 C (600 F). Results showed the molten pyrosulfates to be very corrosive. If $ZnCl_2$ was added, corrosion of the carbon steel was decreased but attack of stainless steel was maintained.

In a study of corrosion of cobalt alloys at higher temperature (~600 C), Luthra (24) has suggested that the major oxidant is $SO_3$. It diffuses in via counter transport of $S_2O_7^{2-}$ and $SO_4^{2-}$. Oxygen (from $SO_3$) is consumed at the scale surface to form $SO_2$. The $SO_2$ (or $SO_3^{2-}$) will diffuse away from the surface. Low $P_{O_2}$ at the metal surface will ensure that the $Cr_2O_3$ film is non-protective. Shores (25) has formulated a mechanism whereby nickel and chromium

could be fluxed from surfaces via pyrosulfate depending on solubilities of the oxides. The role of the pyrosulfates may be similar in the vicinity of the air ports.

**Effects of Chlorides**

It is not essential that pyrosulfate remove the passive film from stainless steel; chloride may do it. Besides forming pyrosulfate via reactions 2 and 3, chlorides may act to deplete the surface of chromium, removing the protective layer. Chlorides may increase the oxidation appreciably above 400 C (750 F) by destroying the protective spinel layer on austenitic stainless steels. When alkalies are also present, chromium is lost from the surface as volatile chromic chloride, increasing the oxidation rate to replace the normal chromium oxide film (14). This may account for the severe attack of stainless steel alloys. Chiang et al. (26) have suggested a process involving $Cr_2(SO_3)_3$ in Ni-Cr alloys. In that process, $Cr_2O_3$ reacts to form $Cr_2(SO_3)_3$ which migrates outward and reprecipitates where $P_{O_2}$ is higher. Further detailed analysis of deposits would be useful to determine the presence and distribution of chloride.

Alexander (27) found that the effect of increasing chloride concentration in mixtures of sulfates and chlorides was more marked with austenitic than with ferritic steels at temperatures of 400-700 C (750 to 1290 F). Apparently, the chloride destroyed the normally protective spinel oxide layer. They observed that when chromium-containing steels were heated with coatings rich in chloride, a green deposit, strongly resembling chromic oxide, $Cr_2O_3$, was formed. This deposit could have been formed only by the volatilization of chromium. They thought that the volatile chromium compound was $CrO_2Cl_2$, $CrCl_3$ or $CrO_3$. The equation which most closely approximated to the observed results was:

$$24\ KCl + 10\ Cr_2O_3 + 9\ O_2 \rightarrow 12\ K_2CrO_4 + 8\ CrCl_3 \qquad (10)$$

This reaction commenced at about 400 C (750 F) and might account for the observation of chromate in smelt deposits and the greenish yellow color observed in deposits from corroded areas of boilers. Reports of low Cl content in the deposits according to Bruno (4), would be consistent with formation of a volatile chlorine compound.

Shinata et al. (28) have studied NaCl induced hot corrosion of stainless steels, and concluded that, in the range 650-900 C (1200-1650 F), chromium is oxidized selectively, leaving a nonprotective $Cr_2O_3$ scale. Corrosion losses increased with increasing chromium content. This raises the question whether a similar process takes place in the recovery boiler at lower temperatures to preferentially attack chromium alloys. If this is the case, then the accelerated wastage of stainless steel from composite tubes may be rationalized in terms of a mechanism involving chloride. Vaughan et al. (16) determined that chloride produced during refuse firing is responsible for serious corrosion. They noted that low temperature corrosion could be attributed to chlorine formed by oxidation of HCl or by conversion of alkali chlorides to sulfates and pyrosulfate. Daniel et al. (29), studying fireside corrosion of refuse-fired boilers, found that mixtures of NaCl + KCl, previously thought to be noncorrosive to furnace wall tubes at 260 C (500 F), became corrosive (especially to stainless steel) when mixed with $FeCl_2$, which forms as a corrosion product on steel surfaces. Resistance to chloride may be very important in preventing recovery boiler corrosion. This question needs to be resolved, and may provide the key to improved performance of air ports.

Chromates, which have been observed in corrosion deposits and offered as evidence of hydroxide corrosion, may arise for many reasons, not necessarily due to reaction of chromium with hydroxides. Equation (10) outlined one pathway for formation of chromate. At higher temperature (975 C), Fryburg et al. (30,31), have indicated that chromium oxide may react to form chromate via:

$$Cr_2O_3 + 2\ Na_2SO_4\ (l) + 3/2\ O_2 \rightarrow 2\ Na_2CrO_4\ (l) + 2\ SO_3\ (g) \qquad (11)$$

Although temperatures are too low on the tube surface, the reaction might occur in the deposit.

## CONCLUSIONS

Results described in the literature to date do not provide unequivocal evidence of NaOH corrosion at recovery boiler air ports and may be based on false premises regarding the presence of NaOH in recovery boilers. The mechanisms of corrosion are not well understood, in large part because the environments in problem areas are poorly characterized. The published information on corrosion of recovery boiler air ports is consistent with an alternative corrosion process involving pyrosulfate and chloride. Work is underway at The Institute of Paper Chemistry to examine ways in which pyrosulfate and chloride might accelerate corrosion of stainless steel near recovery boiler air ports.

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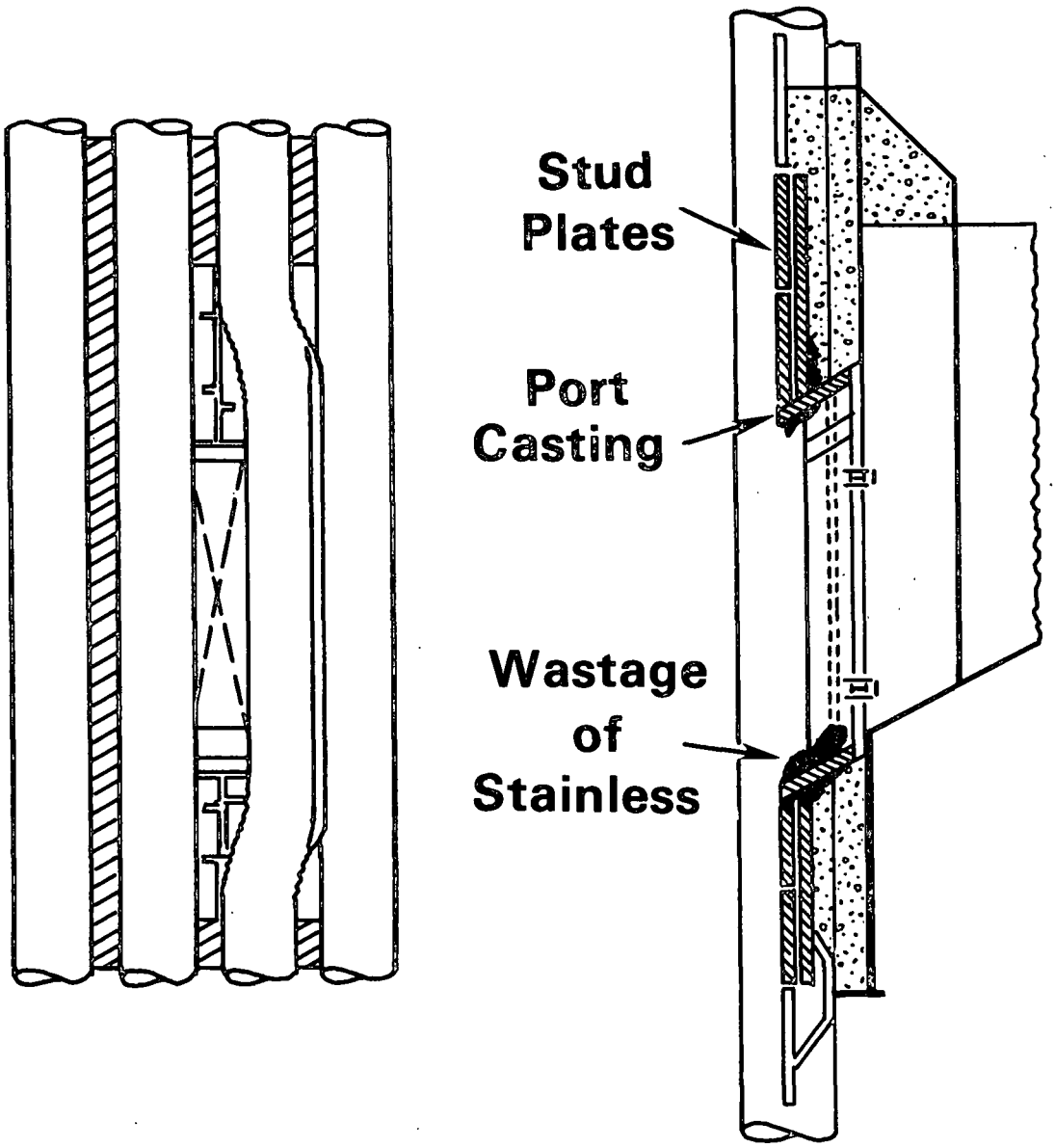


Figure 1. Composite primary air port showing corrosion locations. B&W 1984 design.

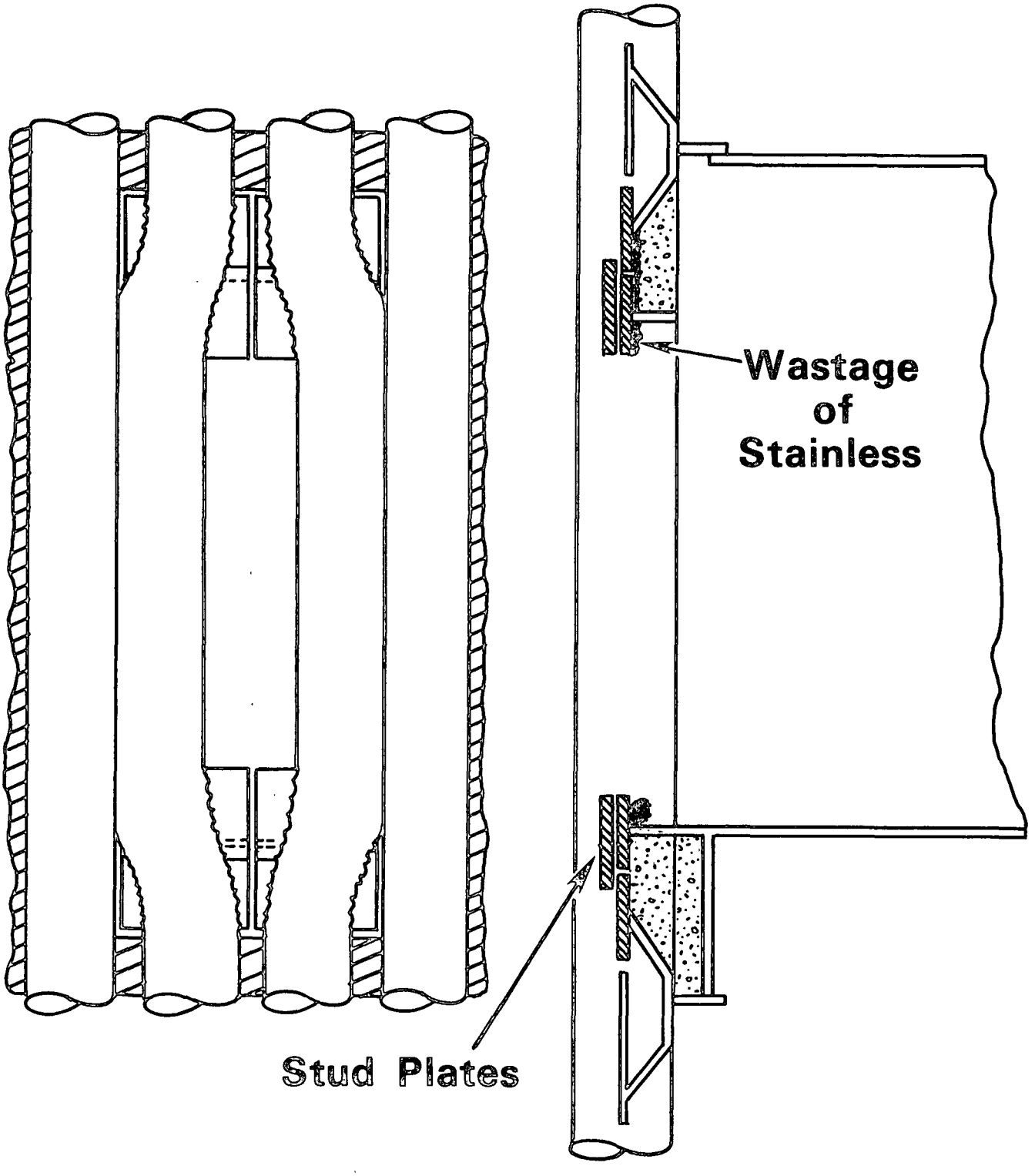


Figure 2. Composite secondary air port showing corrosion locations. B&W 1982 design.

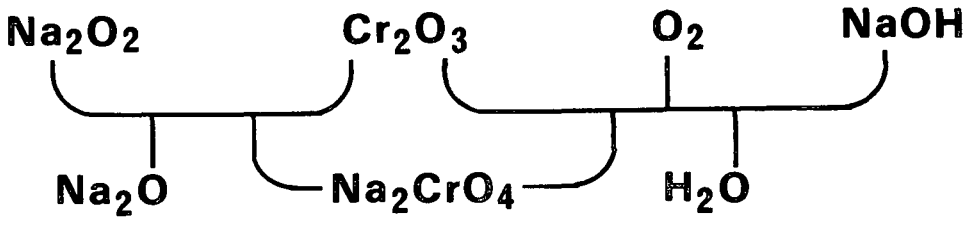


Figure 3. Schematic of hydroxide corrosion mechanism for simplicity, only sodium compounds are illustrated.

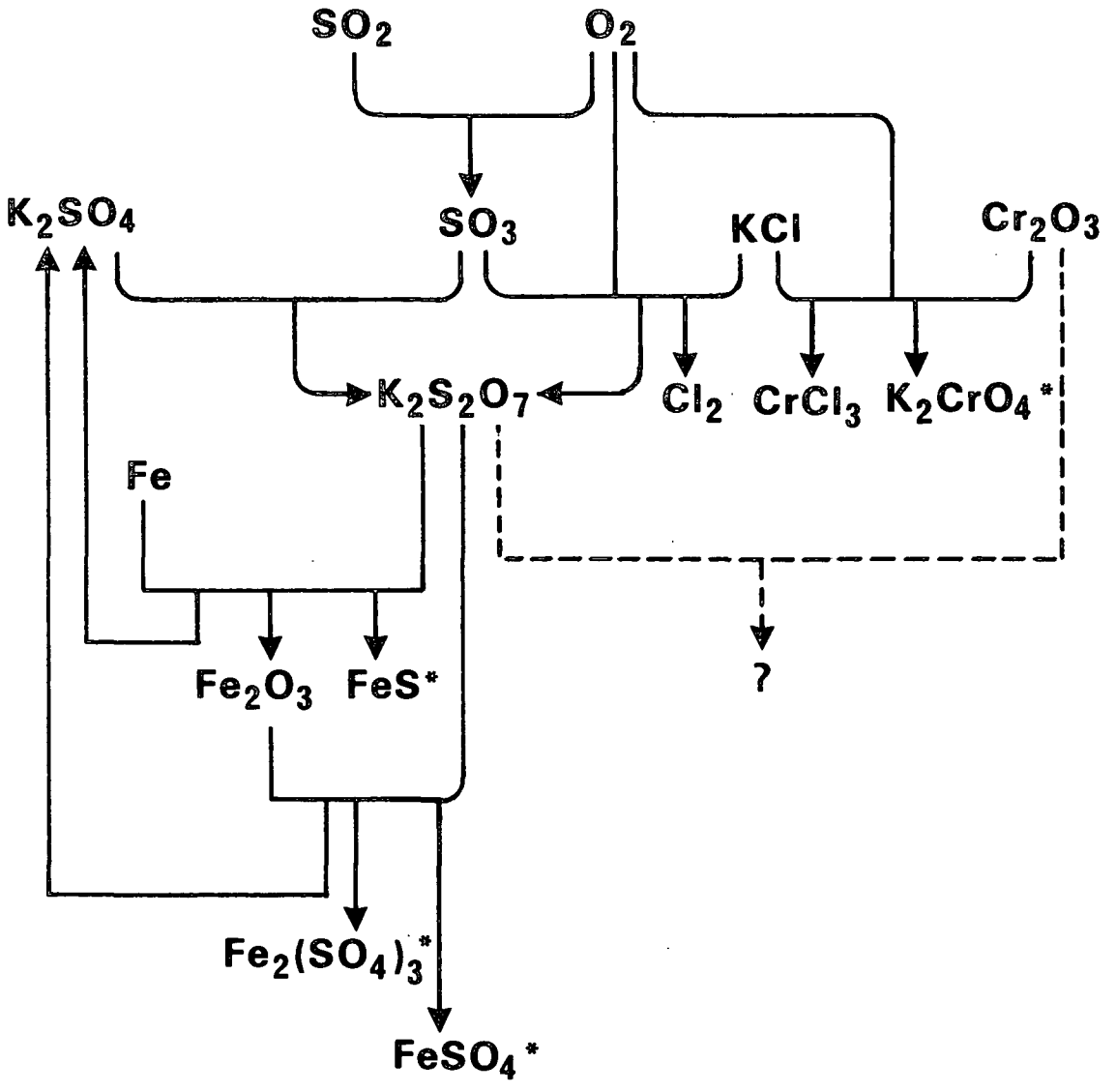


Figure 4. Schematic of pyrosulfate corrosion mechanism. * - Nonprotective. For simplicity, only potassium compounds are illustrated.